

**CIRCULATION COPY
SUBJECT TO RECALL
IN TWO WEEKS**

RHEOLOGICAL PROPERTIES OF MOLTEN KILAUEA IKI
BASALT CONTAINING SUSPENDED CRYSTALS

H. C. WEED
F. J. RYERSON
A. J. PIWINSKII

THIS PAPER WAS PREPARED FOR SUBMITTAL
TO THE ACS SYMPOSIUM ON CHEMISTRY OF MINERAL
MATTER AND ASH IN COAL TO BE HELD ON AUGUST 26-
31, 1984 IN PHILADELPHIA, PA.



Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

RHEOLOGICAL PROPERTIES OF MOLTEN KILAUEA IKI
BASALT CONTAINING SUSPENDED CRYSTALS

H. C. Weed, F. J. Ryerson, and A. J. Piwinski

University of California
Lawrence Livermore National Laboratory
P. O. Box 808, L-201
Livermore, CA 94550

In order to model the flow behavior of molten silicate suspensions such as magmas and slags, the rheological behavior must be known as a function of the concentration of suspended crystals, melt composition, and external conditions. We have determined the viscosity and crystallization sequence for a Kilauea Iki basalt between 1250°C and 1149°C at 100 kPa total pressure and f_{O_2} corresponding to the quartz-fayalite-magnetite buffer in an iron-saturated Pt30Rh rotating cup viscometer of the Couette type. The apparent viscosity varies from 9 to 879 Pa.s. The concentration of suspended crystals varies from 18 volume percent at 1250°C to 59 volume percent at 1149°C. The molten silicate suspension shows power-law behavior:

$$\log |\tau_{yx}| = A_0 + A_1 \log |du/dx|,$$

where τ_{yx} is the shear stress and (du/dx) the shear rate. Since $A_1 \leq 1$, the apparent viscosity decreases with increasing shear rate and the system is pseudoplastic.

In order to understand the flow behavior of molten silicates containing suspended crystals, we need to know the rheological properties of the system as a function of volume fraction of the suspended crystalline phases at appropriate temperatures, oxygen fugacities and melt compositions. Because of the widespread occurrence of silicates, this approach can be applied to magma transport during volcanic eruptions, large scale convective and mixing processes in magmatic systems, and fouling of internal boiler surfaces by coal ash slags in plants burning pulverized coal. The first system we have studied is a basaltic lava from Kilauea Iki, Hawaii, for which we have determined the crystallization sequence and the dynamic viscosity.

Experimental Methods

Starting Material. The starting material for these experiments is Kilauea Iki basalt fragments which have been ground in a tungsten carbide shatterbox to -100 mesh and homogenized by mixing with a paddle and then tumbling for 1.5 hours. This material was then fused in air at 1400°C for about 3.3 hours, quenched in deionized water, rinsed with acetone, and dried under vacuum (15 μ m) at 110°C for 70 hours. The dried material was ground in a boron carbide mortar and pestle and stored in a screw cap glass bottle before use. Light microscopic examination shows that it is clear, free of opaque inclusions, and isotropic under crossed nicols; it is therefore presumed to be glass.

Crystallization Sequence Determination. The starting material for the determination of the crystallization sequence was the homogenized -100 mesh rock powder before fusion. Samples were in the form of spherical beads suspended by surface tension in platinum loops as described by Grove *et al.* (1). They were prepared by pressing about 190 mg of powder into a cylindrical pellet with two or three drops of ethanol as a binder. The diameter of the platinum wire was 0.25 mm and the diameter of the loop about 3 mm. The pellet was fused to the loop by resistive heating of the platinum and then suspended from a platinum bridgewire by an Al₂O₃ connector which insulated it electrically from the bridgewire. The bridgewire was connected across two platinum leads which suspended the entire assembly from the top end fitting of the vertical furnace tube. Oxygen fugacity (f_{O_2}) was controlled by adjusting the mixing ratio of a CO/CO₂ gas mixture flowing through the furnace tube; it was maintained at the quartz-fayalite-magnetite (QFM) buffer (2, 3) and was monitored by recording the EMF from a solid state O₂ sensor in the form of a CaO-stabilized ZrO₂ tube which extended from the lower end of the furnace tube into the hot zone next to the sample (4). Pure O₂ at 110 kPa (1 atm) was circulated inside the ZrO₂ tube as the reference gas. The CO was Matheson C. P. grade or equivalent; the CO₂ was Matheson Coleman Instrument grade or equivalent. Sample temperatures were measured by a Pt/10Rh thermocouple in the hot zone; the thermocouple had been calibrated at the gold point (1063°C). Run times varied from 77 hours at 1270°C to 738 hours at 1130°C. The sample was quenched in deionized water by electrically fusing the bridgewire, which dropped the sample out of the furnace tube. The quenched sample was mounted and polished for analysis. The elemental composition and the phases present were determined by wavelength dispersive X-ray analysis with a fully automated JEOL 733 Superprobe. The weight percentages of the phases present were determined from constrained least squares analysis of the bulk composition and the compositions of the individual phases in each experiment. Weight percentages were converted to volume percentages using estimated densities for the melt and crystalline phases. The calculated volume percentages were compared with those determined by reflected light point counts (1000 pts) of selected experiments. The results of the two methods are in good agreement (Figure 1). The size distribution was not determined.

Viscometry. The starting material for the viscosity determinations was the fused and re-ground glass described above. The viscometer was of the rotating cup Couette type in which the torque and temperature were measured at the bob (5). The cup was cylindrical in shape with a radius of 10.0 mm and a hemispherical bottom. The length of the cylindrical portion was 32.5 mm. The bob was the same shape, with a radius of 8.25 mm and an overall length of 88.1 mm. They were aligned with the hemispheres concentric by means of x-y-z micrometer adjusting screws on the framework which supported the bob. They were fabricated from Pt/30Rh alloy, with an Fe-rich surface produced by heating with a melt (25 weight percent Fe_3O_4 , 75 weight percent Na_2SiO_3) under f_{O_2} corresponding to the iron-wüstite buffer (3). This is intended to minimize Fe transport from the Kilauea Iki melt to the bob and cup (6). Oxygen fugacity was controlled by passing CO/CO_2 gas mixtures through the inner sample tube, which was isolated from the rest of the furnace by water-cooled rotatable mercury seals at the inlet and outlet ends. Flow rates were controlled by vernier throttle valves and ball-type flowmeters; the meter settings were calculated from the manufacturer's published curves (7). The CO/CO_2 ratio was adjusted to given an f_{O_2} corresponding to an extrapolation of the quartz-fayalite-magnetite (QFM) buffer (2,3). The total flow rate was $581 \text{ cm}^3/\text{min}$ corresponding to a linear velocity of 0.9 cm/sec at room temperature and pressure; this had been shown to be large enough to avoid unmixing of the gases due to thermal diffusion effects (8). The CO was Matheson C. P. grade or equivalent; the CO_2 was Matheson Coleman Instrument grade or equivalent. Temperature was measured by a Pt6Rh/Pt30Rh thermocouple which had been calibrated against a pyrometer and standard lamp, with appropriate corrections for intensity losses due to windows and a reflecting prism in the optical train. The accuracy of the temperature measurement was estimated to be $\pm 2^\circ\text{C}$ (9). Torque was measured by a calibrated torsion bar in which the angular deflection and torque were read from four strain gauges mounted on the faces of the bar and connected as a Wheatstone bridge. The unit used in these measurements had a range of $\pm 0.353 \text{ N.m}$ ($\pm 50 \text{ oz.in}$) and digital readout to $7.1 \times 10^{-4} \text{ N.m}$ (0.1 oz.in). The tachometer was a toothed wheel and magnetic pickup with a range of $\pm 999 \text{ rev/min}$, readable to 1 rev/min .

Three types of viscometry experiments were performed: calibration measurements on a standard oil to determine the effective length of the cylindrical column of liquid, isothermal runs on the basalt melts, and polythermal exploratory runs on the basalt melts. Calibration measurements were performed on Brookfield oil ($\mu_0=105 \text{ Pa.s}$) at room temperature and under laboratory atmosphere. The effective length was determined over a range which included the length of the melt samples. Rotation speed was varied from 0 to $\pm 220 \text{ rev/min}$ in 40 rev/min steps, with increasing speed values at even multiples of 20 rev/min and decreasing speed values at odd multiples of 20 rev/min . The positive rotational direction was selected first. At least two torque readings were taken at each value of the rotational speed. The same procedure was followed during isothermal runs on the basalt melts, except that the temperature was noted for each torque

measurement at constant rotational speed in order to monitor the temperature increase due to viscous energy dissipation. The melt sample weight was about 6.65 g, which with an assumed density of 2.78 g/cm³ corresponded to a geometrical length of 14.7 mm for the cylindrical part of the sample. The temperature settings were approached from above by going from room temperature to 1260°C or 1270°C at 100°C/hr to 150°C/hr, then cooling the system at about 1°C/min until the desired temperature was reached. The effect of changing the heating and cooling rates on the viscosity was not explored. Polythermal runs were made at a constant rotational speed, usually 90 to 100 rev/min, and were used to explore the temperature range over which suitable torque readings could be obtained.

Results and Discussion

Crystallization Sequence. Table I shows the major element bulk composition of the starting materials used in our experiments and those of Shaw et al. (10). Kilauea Iki basalt contains less Al₂O₃ and CaO than their material, and much more MgO. Both are within the normal range for basaltic lavas.

Table I. Analyses of Starting Material

Oxide, Wt.%	Kilauea Iki	Shaw <u>et al.</u> (10)
SiO ₂	46.29	50.14
Al ₂ O ₃	10.44	13.37
MgO	17.90	8.20
FeO	11.34*	10.13
Fe ₂ O ₃	-	1.21
CaO	8.49	10.80
Na ₂ O	1.84	2.32
P ₂ O ₅	0.22	0.27
K ₂ O	0.40	0.53
TiO ₂	1.89	2.63
MnO	0.19	0.17
TOTAL	99.90	99.77

*All iron as FeO

The experimental results obtained at the QFM buffer are listed in Table II. and type formulas for the various mineral series in Table III. Olivine and chrome spinel are the only crystalline phases which occur between 1240°C and 1179°C; clinopyroxene and plagioclase feldspar crystallize at approximately 1170°C. The concentration of crystals increases from about 22 weight percent to about 28 weight percent between 1250°C and 1180°C. The liquid line of descent is characterized by a slight SiO₂, Al₂O₃ and alkali enrichment and an FeO and MgO depletion.

The volume percentage of melt as a function of temperature is shown in Figure 1. The break in slope at approximately 1170°C corresponds to the appearance of clinopyroxene and plagioclase feldspar (see Table II.). The volume percentage of melt, V_m, is given by Equations 1 and 2:

$$V_m (\text{Ol}+\text{Chsp}) = 0.157 T(^{\circ}\text{C}) - 114.0, \text{ where } T(^{\circ}\text{C}) \geq 1170, \quad (1)$$

$$V_m = 1.36 T(^{\circ}\text{C}) - 1522.7, \text{ where } T(^{\circ}\text{C}) \leq 1170. \quad (2)$$

Extrapolation of Equation 1 to $V_m=100$ corresponds to $T=1360^{\circ}\text{C}$ for the liquidus. Extrapolation of Equation 3 to $V_m=0$ yields $T=1119^{\circ}\text{C}$ for the disappearance of liquid, the solidus temperature. This is a complex system for which complete phase diagrams are not available; pseudoternary diagrams such as those presented by Grove et al. (1) for similar compositions are generally applicable to this composition.

Viscometry. During viscosity measurements sigmoidal torque versus rotation speed curves are obtained at all investigated temperatures. The curves are linear at rotation speeds less than 0.4 revs/sec, with a positive slope. The curves become concave toward the rotation speed axis at higher rotation rates, indicating pseudoplastic behavior (11). This behavior becomes more pronounced at low temperature as the concentration of suspended crystals increases. Also, at a given rotational speed, the observed torque appears to be slightly lower for negative rotation than for positive rotation. This indicates slight thixotropic behavior of the sample, since positive rotation is used first during experiments. At temperatures near 1149°C , torque measurements are more erratic than at higher temperatures. This may be due to segregation of crystals which causes the sample to rotate intermittently as a rigid body, or due to localized remelting of crystals by viscous heating which increases at lower temperatures.

We have analyzed the results in terms of the power law indicated by Equation 3:

$$\log |\tau_{yx}| = A_1 + A_2 \log |du/dx| \quad (3)$$

where $|\tau_{yx}|$ is the absolute value of the shear stress and $|du/dx|$ the absolute value of the shear rate, calculated by a modification of the method of Krieger and Elrod (12) which applies to non-Newtonian systems. The apparent viscosity, μ , is

$$\mu = \tau_{yx}/(du/dx) \quad (4)$$

The flow curve, Fig. 2, is a plot of Equation 3 showing experimental results obtained at the 1186°C isotherm. Fig. 3 is a log-log plot of apparent viscosity as a function of shear rate at the same temperature. The apparent viscosity decreases with increasing shear rate, which is characteristic for pseudoplastic systems (11). The logarithm of the viscosity at unit shear rate, $\log \mu_0$, is calculated from Equation 3:

$$\log \mu_0 = A_1 \quad (5)$$

Table IV. gives μ_0 as a function of temperature. It varies from 9 Pa.s at 1249°C to 879 Pa.s at 1149°C . The accuracy is estimated as $\pm 15\%$ above 1170°C ; at 1149°C , where the system shows erratic behavior, the accuracy is estimated as $\pm 50\%$.

Table II. Results of Selected Kilauea Iki Liquidus Experiments

Exp't No.	Time (Hrs)	Temp (°C)	Experiment Products	Vol % Melt ^a	Wt % Melt ^b
14	93.0	1240	olivine, chrome spinel, glass	71.8	78.1
9	189.5	1230	olivine, chrome spinel, glass	80.2 ^c	76.1
8	24.0	1219	olivine, chrome spinel, glass	77.3	74.8
10	290.0	1209	olivine, chrome spinel, glass	76.2	74.2
12	289.0	1189	olivine, chrome spinel, glass	63.8	72.5
13	364.0	1179	olivine, chrome spinel, glass	71.8	71.5
16	380.0	1170	olivine, chrome spinel, clino- pyroxene, plagio- clase, glass	69.6	68.5
19	400.0	1160	olivine, chrome spinel, clino- pyroxene, plagio- clase, glass	54.7	53.5
20	400.0	1149	olivine, chrome spinel, clino- pyroxene, plagio- clase, glass	40.7	49.8

- a) Volume percent of melt was determined by a 1000 point mode on metallograph.
- b) Weight percent of melt was determined by constrained least squares analysis of phase compositions.
- c) Volume percent glass was determined by an 850 point mode on metallograph.

Table III. Type Formulae for Mineral Series

Name	Type Formula
Olivine	(Mg, Fe) SiO ₄
Chrome Spinel	AB ₂ O ₄ A = Mg, Fe ²⁺ , Zn, Mn ²⁺ , Ni B = Al, Fe ³⁺ , Mn ³⁺ , Cr
Clinopyroxene	ABSi ₂ O ₆ A = Mg, Fe ²⁺ , Ca, Na B = Mg, Fe ²⁺ , Al
Plagioclase	Ranges from NaAlSi ₃ O ₈ to CaAl ₂ Si ₂ O ₈

Table IV. Apparent Activation Energies from Least Squares Analysis of $\log \mu_0$ vs. $1/(T,K)$ for Kilauea Iki Basalt, Halemaumau Basalt, and Coal Slag X

System	T, °C	Apparent Activation Energy Kcal mol ⁻¹	Standard Deviation Least Squares Fit
Kilauea Iki	1249-1170	123 + 10	.09
	1170-1150	452 + 21	.04
Halemaumau	1130-1158	86 + 9	.12
	1158-1125	635 + 64	.18
Coal Slag X	1482-1330	53 + 1	.013
	1339-1260	424 + 27	.14

The results of least-squares analyses of $\log \mu_0$ vs. $(1/T,K)$ are shown in Figure 4 and Table V. for this investigation on Kilauea Iki basalt, for the work of Shaw on Halemaumau basalt (10,13) and for Corey's report on Coal Slag X (14). The Kilauea Iki data show a sharp increase in slope at 1170°C as indicated by the limiting straight lines above and below this temperature. Below 1170°C, appreciable crystallization occurs as shown in Table II. and Fig. 1, and the system shows strongly pseudoplastic behavior. Shaw's results on Halemaumau basalt (13), which is a Hawaiian basalt quite similar to Kilauea Iki, show a sharp increase in slope at 1158°C. This system shows pseudoplastic behavior at 1125°C and Newtonian behavior at higher temperatures. The results of Corey (14) on Coal Slag X indicate a sharp change in rheological behavior at 1330°C. His original paper gives no details on the calculation of the viscosity results, and no information on the crystallization sequence of the coal slag on which they were obtained. The similarity of the basalt and coal slag data indicates that rheological behavior of the coal slag may be affected by suspended crystalline material at temperatures near 1330°C. A recent study on slagging in large coal-burning furnaces correlates the slagging behavior with ash composition, ash particle morphology, and calculated critical viscosity temperature T_{cv} (15). The methods of the present investigation can be applied in order to measure the critical viscosity temperatures and compositions directly, which should improve the experimental basis for the correlation.

Table V. Apparent Viscosity at Unit Shear Rate (μ_0) vs. Temperature (t, °C) for Kilauea Iki Basaltic Lava

Run No.	T, °C	μ , Pa.s
57	1249	13
63	1249	9
58	1235	9
64	1229	14
59	1220	15
65	1208	25
60	1201	38
66	1188	51
61	1186	52
62	1171	71
67	1170	94
68	1149	879

In both the studies on basalts, the breaks in the slope of the $\log \mu_0$ vs. (1/T,K) curves occur at 20 to 30 volume percent of suspended crystals. The non-Newtonian behavior of these molten silicate suspensions appears to arise from the increasing concentration of suspended crystals in the melt. This suggests that in modeling fluid flow in silicate systems, power law behavior should be considered when the suspended crystal concentration exceeds 20 volume percent.

Acknowledgments

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

Literature Cited

1. Grove, T. L.; Gerlach, D. C.; Sando, T. W. Contrib. Mineral. Petrol. 1982, 80, 160-182.
2. Deines, P.; Nafziger, R. H.; Ulmer, G. C.; Woermann, E. "Temperature-Oxygen Fugacity Tables for Selected Gas Mixtures in the C-H-O System at One Atmosphere Total Pressure"; Bulletin, Earth and Mineral Sciences Experiment Station, No. 88, College of Earth and Mineral Sciences, The Pennsylvania State University, University Park, PA, 1971.
3. Huebner, J. S. In "Research Techniques for High Pressure and High Temperature"; Ulmer, G. C., Ed.; Springer-Verlag, New York, 1971; pp. 123-177.
4. Williams, Richard J.; Mullins, O. "A System Using Solid Ceramic Oxygen Electrolyte Cells to Measure Oxygen Fugacities in Gas-Mixing Systems"; Technical Memorandum TMX-58167, Lyndon B. Johnson Space Center, Houston, TX 77058 1976.
5. Weed, H. C.; Dibley, L.; Piwinskii, A. J. "A High-Temperature Viscometer for Use at 100 kPa"; UCRL-52477, Lawrence Livermore National Laboratory, Livermore, CA 94550, 1978.

6. Grove, T. L. Contrib. Mineral. Petrol. 1981, 78, 298-304.
7. "The F and P Tri-flat (Low Flow Rate) Variable Area Flowmeter Handbook; Application, Sizing, and Calibration Prediction Data", Catalog 10A9010, Fischer and Porter Co., Hatboro, Pa, Pub. 13317, September, 1959.
8. Darken, L. S.; Gurry, R. W. J. Am. Chem. Soc., 1945, 67, 1398-1412.
9. Weed, H. C.; Piwinski, A. J.; Dibley, L. L. "Experimental Study of the Dynamic Viscosity of Some Silicate Melts to 1953K at 150 kPa", UCRL-52757, Lawrence Livermore National Laboratory, Livermore, CA, 94550, 1979, p. 2.
10. Shaw, H. R.; Wright, T. L.; Peck, D. L.; Okamura, R. Amer. Jour. Sci. 1968, 266, 225-64.
11. Skelland, A. H. P. "Non-Newtonian Flow and Heat Transfer"; J. Wiley and Sons, New York, 1967, pp. 5-12.
12. Krieger, I.; Elrod, H. J. Appl. Phys. 1953, 14, 134-6.
13. Shaw, H. R. Jour. Petrology 1969, 10, 510-535.
14. Corey, R. C. "Measurement and Significance of the Flow Properties of Coal-Ash Slag"; Bulletin No. 618, U. S. Bureau of Mines 1964, pp. 1-64.
15. Hazard, H. R. "Influence of Coal Mineral Matter on Slagging of Utility Boilers"; EPRI CS-1418, Project 736, Final Report, Electric Power Research Institute, Palo Alto, CA 94304, 1980.

Figure 1. Volume percent and weight percent melt as a function of temperature for Kilauea Iki basalt. Vertical bars indicate two standard deviations.

Figure 2. Least squares fit of $\log(\text{Shear Stress})$ vs. $\log(\text{Shear Rate})$ for Kilauea Iki basalt at 1186°C . Vertical bar indicates two standard deviations.

Figure 3. $\log(\text{Apparent Viscosity})$ vs. $\log(\text{Shear Rate})$ for Kilauea Iki basalt at 1186°C . Vertical bar indicates two standard deviations.

Figure 4. Least squares analysis of $\log(\text{Viscosity})$ vs. reciprocal temperature. Present study \circ ; Shaw (13) \triangle ; Corey (14) \square . Vertical bars indicate two standard deviations.







